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Magnetic ordering within the layered terbium carbide iodide, $Tb_2C_2I_2$

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Abstract

The compound $Tb_2C_2I_2$ crystallizes with a layered structure (space group=*C2*/*m*), which has a close-packed arrangement of I–Tb–Tb–I slabs. C_2 units are located within the Tb octahedral voids. Powder magnetic susceptibility measurements suggest two antiferromagnetic ordering transitions below 90 K. From the refinement of neutron powder diffraction patterns, the Tb moments order with a propagation vector $\boldsymbol{k}$=(0,0,0). The refined Tb moments are 8.0(1) μ_B at 10 K, and they are aligned antiferromagnetically in the **ac** plane. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: $Tb_2C_2I_2$; Magnetically ordered materials; Neutron diffraction; Phase transition; Rare-earth metal carbide halide

1. Introduction

Since the first rare-earth metal carbide bromide, $Gd_2C_2Br_2$, was synthesized, much study has been devoted to the properties of structurally isotypic non-magnetic rare-earth metal carbide halides, $RE_2C_2X_2$ (RE=Y, La, Lu; X=Cl, Br, I) because of their superconducting behavior [1]. The $RE_2C_2X_2$ crystallize with a layered structure consisting of slabs of double-layers of close-packed rare-earth metal atoms which are sandwiched between layers of halogen atoms. Such slabs stack along the crystallographic *c* axis to form alternating double-layers of metal and halogen atoms. Two different stacking sequences (1s- and 3s-type) have been found which differ

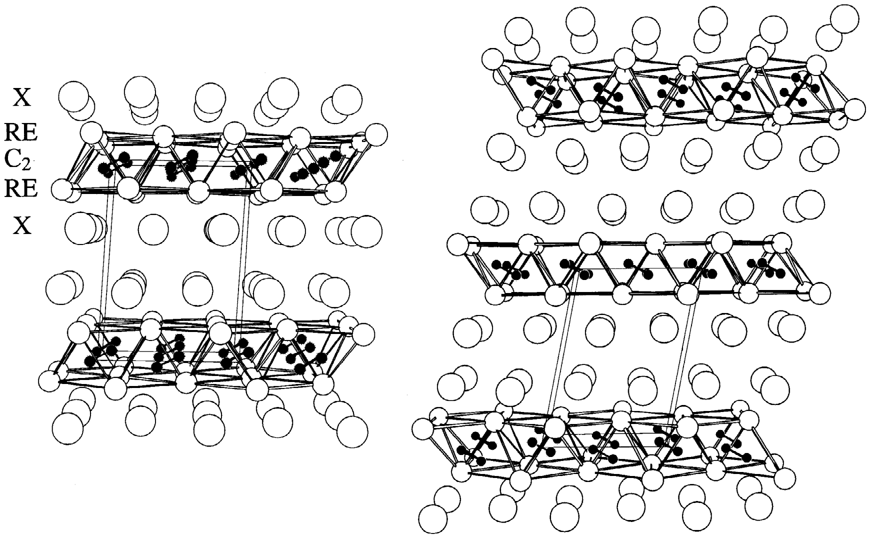

Fig. 1. Perspective view of the structures of $RE_2C_2X_2$ (1s stacking variant left and 3s right).

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in the number of double-layers necessary to build a unit cell as shown in Fig. 1 [2,3]. C_2 dumbbells are located in the octahedral voids within the metal atom double-layers. Backbonding from the C_2 group to the metal atoms leads to metallic conductivity, which consequently may be expected to be strongly anisotropic, and essentially confined to the metal–carbon atom layers [4,5].

While the properties of superconducting compounds of the system $RE_2C_2X_2$ are now well established, the properties of the compounds containing magnetic rare-earth metals are still largely unknown. Due to the pronounced layered characteristic of the crystal structure, the magnetic properties of the rare-earth metal carbide halides should be strongly anisotropic.

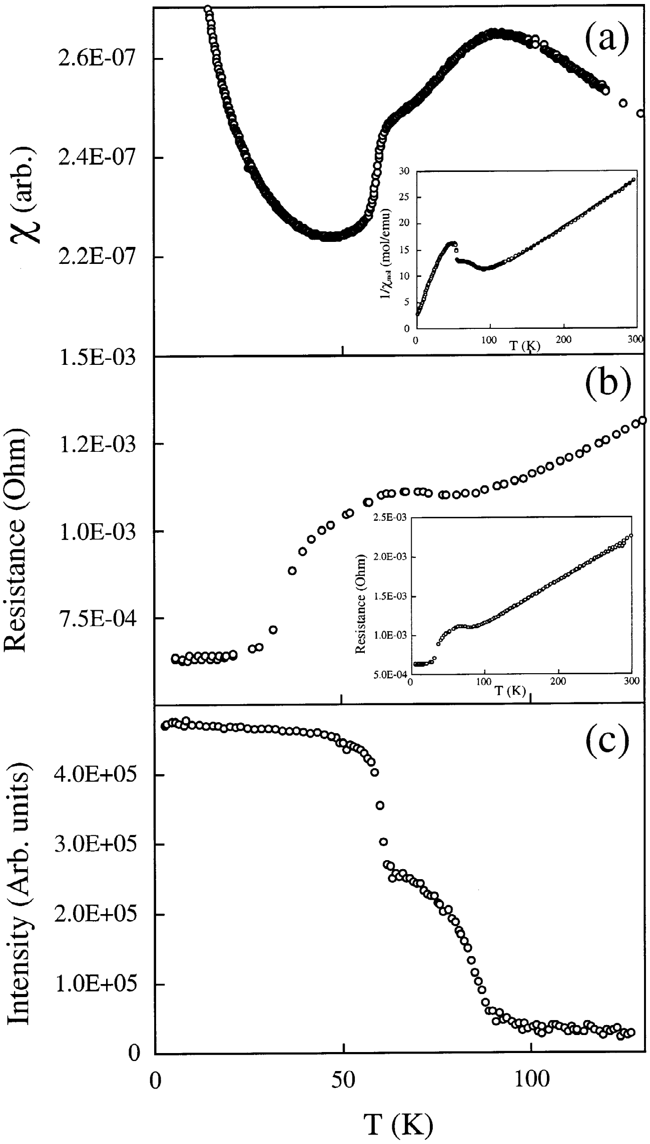

Fig. 2. (a) Magnetic susceptibility of powder sample of $Tb_2C_2I_2$, (b) temperature dependence of resistivity of a sintered pellet, (c) temperature dependence of the integrated magnetic intensity in the vicinity of the reflection (1 0 0), data taken at D20 (ILL, Grenoble, France).

For example, the exchange coupling is predominantly within the rare-earth metal layers, and evidence for low dimensional magnetic behavior has been seen in susceptibility and resistivity measurements on $Gd_2C_2Br_2$ ($T_N \approx 40$ K) [3].

Recently, we have successfully synthesized polycrystalline samples of pure 1s-type $Tb_2C_2I_2$ and are currently studying their magnetic properties. Susceptibility and resistivity data are presented and the low temperature magnetic structure is refined from neutron powder diffraction patterns.

2. Experiment

$Tb_2C_2I_2$ polycrystalline samples were synthesized from the reaction of Tb metal, TbI_3 and carbon powder. Reactions were run at 1050°C for 10 days in sealed Ta capsules that were in turn encased in evacuated silica tubes. Preparation of TbI_3 and sample handling are described in detail elsewhere [4]. The products were characterized with a STOE X-ray powder diffractometer.

The susceptibilities of powder samples were determined with a Quantum Design SQUID magnetometer (MPMS) between 2 and 300 K in a magnetic field of 1 T. Measurements were performed on ~70 mg samples contained in dried quartz glass ampoules in He atmosphere. Resistivity measurements of sintered pellets (5 mm diameter and 1 mm thickness) were carried out using the van der Pauw method.

Neutron powder diffraction measurements were performed with the DMC powder diffractometer ($\lambda=2.556$ Å) at the Paul-Scherrer-Institut (Villigen, Switzerland), and the D20 high-flux powder diffractometer ($\lambda=2.41$ Å) at the ILL (Grenoble, France). Neutron powder diffraction patterns were recorded at the lowest possible temperatures (10 K, DMC and 2 K, D20) and at several intermediate temperatures up to, and above, the transition temperature. Powder patterns were collected on polycrystalline samples of ~5 g which were encapsulated in a thin-walled vanadium container. Dried helium at 1 bar was used in the vanadium container as heat exchange gas.

Refinements of the nuclear and magnetic structures were carried out with the Rietveld method using the Fullprof program [6]. Due to the resolution limit of the instruments, the refinement of the nuclear structure was not adequate, and for the refinement of the magnetic structure, atomic positional parameters were fixed to the data of $La_2C_2I_2$ [4]. From the 400 data points containing 36 nuclear and 110 magnetic contributing reflections, 16 parameters were refined, of which 11 were global (one instrumental, six background, three profile and one asymmetry parameters) and seven local (one overall scale factor, four lattice parameters and two components of magnetic moment).

3. Results and discussions

As mentioned in the introduction, two types of stacking variants (1s- and 3s-type) exist in the series of compounds, $RE_2C_2X_2$ (RE=Y, La, Lu; X=Cl, Br, I), and these two variants can be synthesized under slightly different reaction conditions, e.g. adding some excess carbon results in the 3s-type compound [4]. For the light rare-earth metal carbide iodides (La–Gd), two different variants could be selectively synthesized by varying the amount of carbon powder added. For the heavy rare-earth metal compounds, however, including Tb, only the 1s-type can be synthesized in the case of the iodides. 1s-$Tb_2C_2I_2$ shows antiferromagnetic ordering with two transitions, a broad one around 90 K and a sharp transition at 60 K (Fig. 2(a)). The upturn below 50 K is assigned to paramagnetic impurities. Two transitions are also indicated by the electrical resistivity measurement showing anomalies at the relevant temperatures as shown in Fig. 2(b).

The temperature dependence of the neutron powder diffraction of $Tb_2C_2I_2$ was measured using D20 (ILL, Grenoble, France). Fig. 2(c) shows the temperature dependence of the integrated magnetic intensity around the reflection (1 0 0) which is the most intense magnetic peak. A sharp transition at 60 K and a broad one around 90 K are visible. Above 90 K diffuse magnetic scattering was observed, most likely due to short-range correlations in the Tb layers. A detailed analysis of these features is in progress [7].

The neutron powder diffraction data collected at DMC at 200 K were used to confirm the nuclear structures. The Rietveld refinement results for $Tb_2C_2I_2$ are shown in Fig. 3(a). The pattern was refined on the basis of the space group *C2/m*. Initially the Rietveld refinement had been started assuming the co-presence of the 1s- and the 3s-structure type, but this sample turned out to be of the 1s-type stacking variant only.

The additional reflections at 10 K (Fig. 3(b)) are due to coherent magnetic scattering of the Tb^{3+} ions. These magnetic peaks can be indexed based on the commensurate propagation vector $\boldsymbol{k}=(0,0,0)$. The Shubnikov group is $P2/m'$ ($a=7.217(3)$ Å, $b=3.896(1)$ Å, $c=10.424(5)$ Å and $\beta=93.54(2)$ at 10 K). The final results of the Rietveld refinement of the pattern at 10 K are shown in Fig. 3(b) ($R_{\mathrm{Bragg.}}=6.48$ and $R_{\mathrm{Mag.}}=5.91$). The magnetic moment refines to 8.0(1) μ_B which is somewhat smaller than the possible maximum moment ($J=6$, $g_J=3/2$) of a Tb^{3+} ion (9 μ_B).

The Tb moments were found to be aligned in the **ac** plane with an antiferromagnetic arrangement as displayed in Fig. 4. Closer inspection reveals the moment orientation to be antiparallel (antiferromagnetic) through the C-C dumbbells and pointing along the direction of the C-C dumbbells.

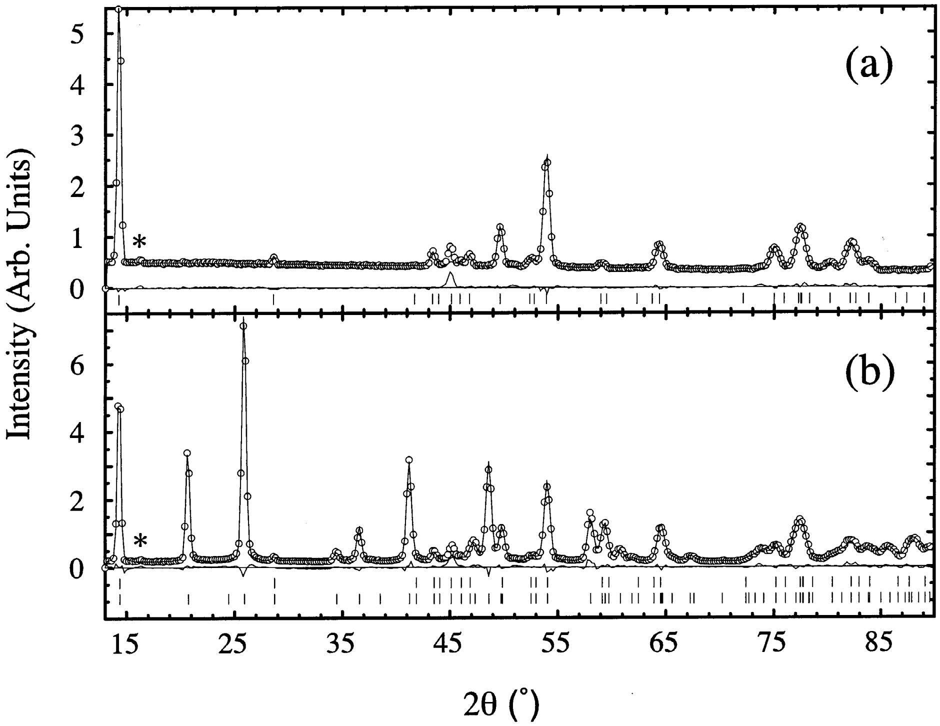

Fig. 3. Observed (○), calculated (full line) and difference neutron powder diffraction patterns for $Tb_2C_2I_2$ (1s type) (a) at 200 K and (b) 10 K, data taken at DMC (PSI, Villigen, Switzerland). A peak marked (*) around 16° is attributed to a phase of TbOI, which is not included in the refinement. A small deviation in the patterns at 200 and 10 K between 44.2 and 45.6° remains unidentified.

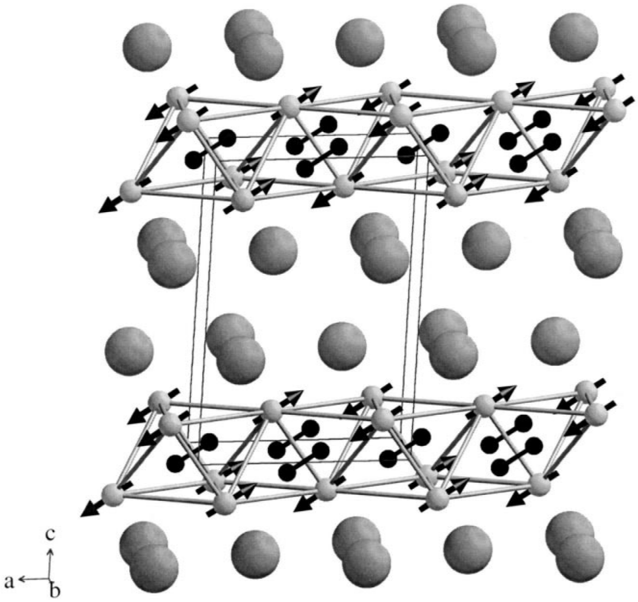

Fig. 4. Magnetic structure of $Tb_2C_2I_2$ as refined from the 10-K dataset. The arrows represent the Tb magnetic moments. Large, medium and small spheres represent I, Tb and C, respectively.

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